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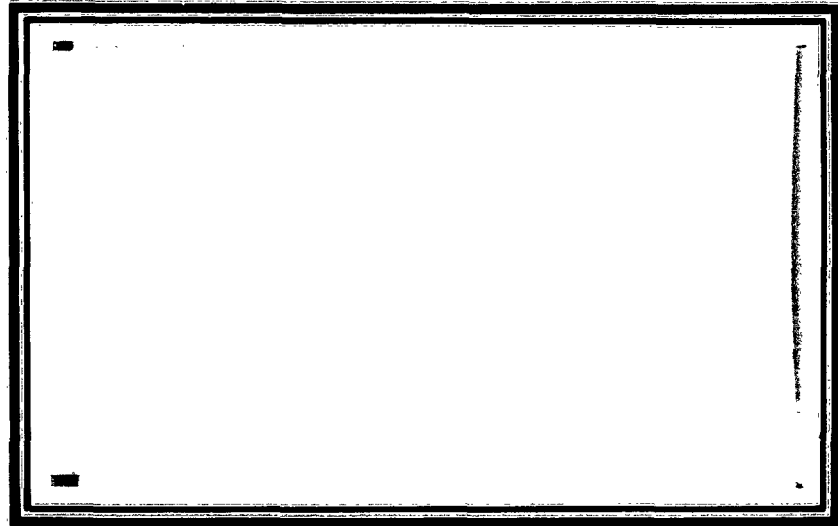
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AD No. 29

**TECHNICAL REPORT****MATERIAL LABORATORY****NEW YORK NAVAL SHIPYARD****BROOKLYN 1, NEW YORK**

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SYNTHESIS OF THERMALLY STABLE
SILARYLENE POLYMERS

Lab. Project 6135, Progress Report 8
Subproject R-007-03-03, Task No. 1000
Identification No. 25-1000-3

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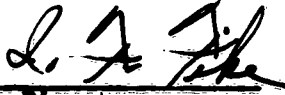
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ABSTRACT

Significant advances have been achieved in the development of thermally stable semi-inorganic polymers with potentially useful end-item characteristics. Techniques are described for the synthesis of novel silarylene polymers and monomers showing pyrolytic resistance far superior to that exhibited by commercially available macromolecular substances. Linear and cyclic silbiphenylene polymers prepared in this program show weight losses when heated at 180°C/hr. to 500°C of approximately 13 and 18%, respectively, as compared to that shown by commercial dimethylpolysiloxane gum which is completely volatilized at 350°C when similarly treated. In addition, results of exploratory curing processes are given which indicate the potential suitability of FeCl_3 and a mixture consisting of benzoyl peroxide and cobalt naphthenate as curing agents for a perphenylated polysiloxane and a linear silbiphenylene polymer, respectively. Additional crosslinking mechanisms will be investigated to further improve thermal stability of the polymeric products without sacrifice of engineering properties.

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	2
ADMINISTRATIVE INFORMATION	4
REFERENCES	4
INTRODUCTION	4
OBJECT	5
RESULTS AND DISCUSSION	5
SUMMARY	9
FUTURE PLANS	9
BIBLIOGRAPHY	10
DISTRIBUTION LIST	

TABLES

- 1 - Effects of Curing Agents on Linear Silbiphenylene Polymer
- 2 - Effects of Curing Agents on Perphenylated Siloxane Polymer

APPENDIX

- A - Experimental

A-1 - A-2

ADMINISTRATIVE INFORMATION

1. The silarylene syntheses studies covered in this report were conducted at the Material Laboratory during January 1960 through July 1962. The cross-linking studies were made during the period 1 July through 30 September 1962.
2. In paragraph 6 of a previous report⁷, the Material Laboratory indicated that it has successfully synthesized small experimental quantities of two polymers which demonstrated high thermal stability. It was recommended that arrangements be made for the commercial preparation of pilot batches of these experimental polymers for subsequent modification and formulation into prototype end-items for diverse naval applications. Accordingly, preliminary inquiries have been made of several manufacturers of organic chemical specialties regarding cost and capability for preparing the silbiphenylene polymer. Similarly inquiries are underway to promote commercial preparation of the triphenylsilanol necessary for the production of practical quantities of the high temperature resistant resin resulting from the interaction of triphenylsilanol and $AlCl_3$. It is expected that precise information along these lines will be available shortly for transmittance to and action by the Bureau.
3. These studies are being conducted at the Material Laboratory in the Organic Chemistry Section (Code 974), under the supervision of B.B. Simms, Section Head. Bureau of Ships cognizance of this work is administered through Program Manager E.A. Bukzin (Code 342A) and Project Engineer W.B. Shetterley (Code 634C4).

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- (b) MATLAB Tech Director Memo 902/hk of 5 Oct 1959
- (c) MATLAB Tech Director Memo 912/MJC:hk of 30 June 1960
- (d) MATLAB Tech Director Memo 903/EJJ:hk of 30 June 1961

INTRODUCTION

4. To develop elastomers and resins for use by the Navy in applications requiring functional materials with high resistance to pyrolytic degradation the Material Laboratory is conducting a continuing semi-inorganic polymer synthesis program under the authority of reference (a). The results of earlier phases of these studies are presented in previous reports¹⁻⁷. In general these data indicate the importance to the development of new thermally resistant polymers of incorporating ring and/or cyclic structures into the molecules. For example, the reaction of triphenylsilanol and aluminum chloride resulted in the synthesis of a novel open-chain siloxane polymer with branches comprised of cyclic trimer groups⁶. This semi-inorganic polymer is unusually resistant to degradation by heat, showing a weight loss of only about 9% when heated to 500°C at 180°C/hr. On the basis of these studies, the Material Laboratory's efforts in this program are now being directed towards the development of techniques for utilizing highly resonating ring and/or cyclic structures as building blocks for the synthesis of high-temperature stable polymers. In this connection, studies along these lines were made under the authority of references (b)-(d), and are continuing as authorized by reference (a). The high-lights of these investigations are described in this report. In addition, data are presented on the results of preliminary efforts to develop curing processes for the high-temperature resistant resin obtained from the reaction of triphenylsilanol and aluminum chloride⁶ and for a pyrolytically stable silbiphenylene polymer prepared under

the references (b)-(d) program. This work was undertaken to provide new materials with chemical, physical, and mechanical properties that are suitable for end-item use over a wide range of naval applications.

OBJECT

5. These studies were made to develop techniques and methods for the synthesis of novel heat resistant silarylene polymers for use in the fabrication of thermally stable end-items required by the Navy. In addition, investigations were initiated to develop suitable crosslinking reactions to prepare thermally stable polymers based on perphenylated polymers containing main-chains with Si-O-Si or Si-C₆H₄-C₆H₄-Si linkages.

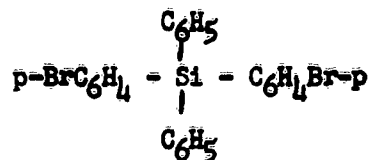
RESULTS AND DISCUSSION

6. In general, aromatic compounds exhibit greater resistance to thermal attack than do aliphatic and alicyclic hydrocarbons of comparable molecular weight. Several investigators^{8,9} have reported that aliphatic and alicyclic hydrocarbons are protected to some extent against thermal degradation by the incorporation of aromatic compounds. Polymers based on aromatic nuclei in the main-chains, as in the case of polystyrene and polyethylene terephthalate, are more resistant to thermal degradation than are similar materials comprised only of alkyl constituents. For the silicones, ethylphenyl-¹⁰ and methylphenylsiloxane¹¹ polymers are serviceable up to maximum air temperatures of about 250 and 300°C, respectively. On the other hand, polymers with only phenyl substituent groups resist degradation in air for several hours at 400-500°C.,⁶ while the methylpolysiloxanes are useful to about 200°C.¹² The protective effects of the aromatic groups are attributed, generally, to their ability to resist and inhibit molecular degradation due to bond rupture by the direct absorption of incident thermal energy or by acceptance of such energy by transfer from less heat resistant aliphatic structures. These considerations suggest that outstanding thermal stability characteristics might be exhibited by polymeric materials prepared by incorporating silicon-aryl structures in the macromolecular backbone or main-chain. In this connection, a variety of organosilicon polymers containing alternate aryl rings and silicon atoms as the structural framework might be prepared by suitable choice of substituent groups. For example, Clarke¹³ has reported the synthesis of polymers having the structure C₆H₅Cl₂(SiC₆H₄SiCl₂)_n C₆H₅ by heating (C₆H₅)₂SiCl₂ at 210-300°C in the presence of a catalytic amount of AlCl₃. Barry¹⁴ prepared similar products by heating a mixture of methylphenylchlorosilanes in the presence of BCl₃. Substances with SiC₆H₄-C₆H₄-Si structures and alkyl substituent groups have been prepared by treating (CH₃)₂SiCl₂ with dilithium compounds¹⁵. However, the technical literature provides little, if any, information regarding the thermal stability of materials of this type. Accordingly, the Material Laboratory has been utilizing halogen metal inter-conversion reactions to synthesize silarylenes for such evaluations. Specific experimental details of the reactions used are presented in Appendix A. The nature of the resulting products, and their thermal stabilities are discussed in the following sections.

7. Reactions of Diphenyldichlorosilane and Lithium Benzene Compounds:

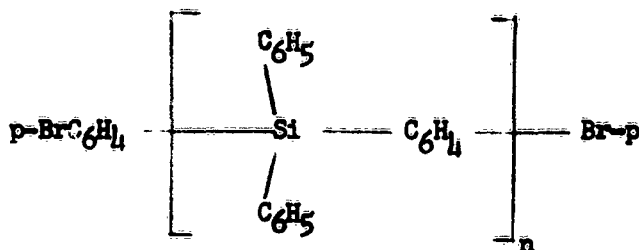
The reaction of p-dibromobenzene and n-butyllithium produced a mixture of 1,4-bromolithium - and p-dilithiumbenzene. Subsequent treatment of the mixture of aryllithium compounds with diphenyldichlorosilane yielded the compound bis-

(p-bromophenyl) diphenylsilane



(I)

and a low molecular weight silphenylene polymer having the probable structure.



(I.a)

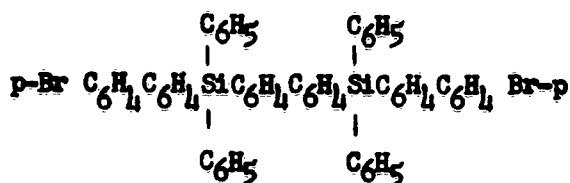
where n is an average of about 3.

The thermogravimetric analysis (TGA) thermograms of these substances indicate that the monomer (I) and polymer (I.a) lose 50% of their volatilizable components at approximately 410 and 510°C, respectively, when heated in air at 180°C/hr. These data suggest, therefore, that the pyrolytic resistance of such silarylene products might be improved by increasing the degree of polymerization.

8. Reactions of Diphenyldichlorosilane and Lithium Biphenyl Compounds:

a. Synthesis of 4,4'-Bis [p-bromo-p'-biphenyl(diphenyl) silyl] biphenyl(II):

The interaction of 4,4'-dibromobiphenyl and n-butyllithium follows by the addition to the reaction mixture of diphenyldichlorosilane yielded compound II.



II

The infrared spectrum of the product shows absorption peaks in the 5-6u region and at 12.3u which are characteristic frequencies for p-substituted benzene derivatives. Absorption bands are exhibited also at 13.58 and 14.35u which are assigned to C-H out-of-plane bending vibrations normally observed in the infrared spectra of monosubstituted benzene compounds.

The TGA thermogram of II shows a loss of 50% of its volatilizable components at approximately 525°C, which is higher by approximately 115 and 15°C than the temperatures for corresponding volatile losses shown by compound (I) and the silphenylene resin (Ia), respectively. On this basis, silbiphenylene compound II is considered to be more thermally resistant than the monomeric and polymeric silphenylene substances discussed previously.

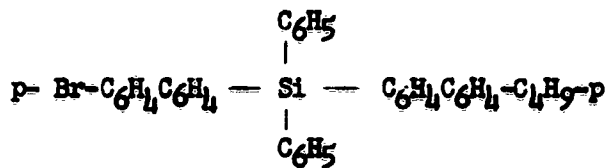
b. Synthesis of Linear Silbiphenylene Polymer and p-Bromo-p'-biphenyl-p-butyl-p'-biphenyldiphenylsilane:

The presence of reactive bromine atoms in II suggests strongly the possibility of additional halogen-metal interconversion reactions. Since the pyrolytic stability of the silphenylene substances appears to be influenced by the number of repeating units in the main-chains, such reactions could provide silphenylene materials of high molecular weight which would exhibit superior resistance to thermal degradation. In view of the excellent resistance to thermal attack demonstrated by II, and its structural bifunctionality in the form of two reactive bromine atoms on the chain ends, this substance was considered to be suitable for use as an intermediate product in the synthesis of new and more heat resistant silbiphenylene polymers.

To expedite the preparation of these polymers, the experimental procedure was modified. Diphenyldichlorosilane was interacted with 4,4'-dilithium biphenyl and the reaction mixture was treated with 4-bromo-4'-lithium biphenyl. This reaction sequence produce a very-light yellow, hard, brittle, ether insoluble resinous polymer having the probable structure,



where n, the average number of chain units, is about 4.5. The reaction also yielded an ether soluble fraction. About 85% of the crude ether soluble product was found to be a very light yellow, petroleum ether insoluble, hard solid substance, which was determined by elemental and infrared spectrophotometric analyses to be IV.



(IV)

The remainder of the ether soluble fraction was determined to be unreacted 4,4'-dibromobiphenyl.

The thermogravimetric data of the several fractions obtained show that the ether insoluble resin fraction (III) loses 50% of its volatilizables at 610°C. when heated at 180°C/hr., which is approximately 100°C higher than the comparable 50% volatilization temperature shown by the silbiphenyl monomer (II). Under similar treatment, (IV) shows the 50% volatilizables loss at 550°C. At 500°C, the silbiphenylene polymer shows a weight loss of approximately 13% of its original weight, and appears to be unchanged structurally when examined by infrared spectrophotometry.

It is evident from these data that the pyrolytic stability of silbiphenylene substances is superior to that shown by similar silphenylene products. As in the case of the silphenylenes, the resistance to heat attack of the silbiphenylene materials are influenced by the number of repeating groups in the main-chains of the molecules.

c. Synthesis of Cyclic Silbiphenylene Polymer:

In a similar reaction involving the interaction of larger quantities of 4,4'-dibromobiphenyl, n-butyllithium, and diphenyldichlorosilane a cyclic substance was obtained having molecules with probable structures of $(\text{Si}(\text{C}_6\text{H}_5)_2 \cdot \text{C}_6\text{H}_4\text{C}_6\text{H}_4)_n$. The reaction also produced an oily product which was found to be a mixture of diphenylpolysiloxane and n-butyl bromide.

The TGA thermogram shows the cyclic silbiphenylene product loses 50% of its volatilizable components at about 580°C when heated at 180°C/hr. The substance only loses 18% of its original weight when heated to 500°C. These data are additional evidence of the generally superior resistance of silbiphenylene products to pyrolytic degradation.

9. Curing Studies:

While the linear silbiphenylene resin discussed herein might be developed into useful protective coatings by the selective modification with various solvents, pigments, and additives, these coatings would have only limited use since the resin softens at 150-160°C. To extend the thermal stability range of such products, exploratory investigations were undertaken to devise techniques for crosslinking the molecules to produce infusible three dimensional networks. Similar studies also were made of the thermally stable polymeric product obtained from the reaction of triphenylsilanol and aluminum chloride⁶ which softens at 75-85°C. The selection of crosslinking agents is dependent primarily on the nature of the reactive sites on the polymer chains being investigated. In this connection, the absence of the active groups suitable for crosslinking purposes limits the choice of curing agents to metallic oxides, organic peroxides, and Lewis acids, which induce crosslinking through bond cleavage mechanisms. The results of initial studies along these lines with the linear silbiphenylene polymer are presented in Table 1. These data indicate that a curing agent consisting of a mixture of benzoyl peroxide and cobalt naphthenate shows promise as a curing agent for the polymer, and that additional studies with these materials are warranted. The silbiphenylene polymer is not appreciably crosslinked when treated similarly with FeCl_3 , benzoyl peroxide, or a mixture of benzoyl peroxide and PbO .

The effects of crosslinking agents on the resin obtained from the reaction of triphenylsilanol and aluminum chloride are shown in Table 2. These data indicate that an infusible polymer network is formed when the resin is treated with FeCl_3 . The degree of crosslinking appears to increase with the concentration of FeCl_3 and decrease as the temperature and time of cure increases. When the polymer is treated for 6 hours at 140°C with 2.0 or 10.0 P.H.R. of FeCl_3 , the

degree of network formation is 44.6 and 60.8%, respectively. The siloxane polymer is not appreciably crosslinked when treated similarly with Al_2O_3 , TiO_2 , benzoyl peroxide, and mixtures of benzoyl peroxide with cobalt naphthenate or PbO .

SUMMARY

10. Techniques have been described for the synthesis of new polymers and intermediate compounds containing perphenyl-p-silarylene molecular configurations. Information also has been provided concerning the properties of these materials, with particular emphasis on their high-temperature resistance. The aryl groups of the main-chains stabilize these semi-inorganic substances and provide them with unusually good resistance to degradation by heat. In fact these silarylene products are far more thermally stable than commercially available polymeric materials. Substances with biphenyl groups are more pyrolytically resistant than similar products with benzene rings in the main-chains. The protective effects provided by these aryl groups appear to increase as the degree of polymerization increases. The bromine atoms in the molecules have a useful function since they can serve as active sites which are capable of undergoing reactions that could produce polymers with longer chain lengths or modified structures.

Finally, the results of exploratory investigations to develop methods for crosslinking perphenylated silbiphenylene and siloxane resins are described. The most suitable crosslinking agent for providing the silbiphenylene with a wider variety of engineering characteristics appears to be a mixture comprised of benzoyl peroxide and cobalt naphthenate. For the perphenylated siloxane resin, high degrees of crosslinking are obtainable by heating the resin with 2 - 10 P.H.R. $FeCl_3$ under pressure.

FUTURE PLANS

11. On the basis of the superior thermal resistance of the silarylene products described herein, efforts in the heat stable semi-inorganic polymer synthesis program for the development of new macromolecular products containing ring and cyclic structures in the molecular backbone are continuing.

Additional crosslinking studies are now underway to provide those polymers that exhibit excellent thermal stability with a wider variety of engineering properties and end-item applications.

Studies involving the synthesis of polymers with $Si - O$ and $Zr - O$ bonds in the main chain are nearing completion. Results of these studies will be reported to the Bureau on or about 1 April 1963.

A. D. Delman

A.D. DELMAN
Principal Investigator

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APPENDIX A

Experimental

A. Reactions of Diphenyldichlorosilane and Lithiumbenzene Compounds:

A. solution consisting of 31.8g (0.16 mole) of p-dibromobenzene dissolved in 120 ml. of anhydrous ethyl ether was added dropwise during 2 hrs. to 200 ml. of a mixture of pentane and heptane containing 0.2 mole of n-butyllithium at -10°C under a nitrogen atmosphere. Then, 13.0g. (0.05 mole) of diphenyldichlorosilane was added dropwise during 1 hr. with vigorous stirring at room temperature. After refluxing for 8 hrs. and standing at room temperature overnight the mixture was hydrolyzed with dilute HCl and extracted with ether. The ether layer was separated, dried over anhydrous Na_2SO_4 , and extracted with ethyl alcohol to give 4.0g of bis (p-bromophenyl) diphenylsilane, m.p. 163°C . (Found: Si, 5.7 and Br, 32.0, Calc. for $\text{C}_{21}\text{H}_{18}\text{Br}_2\text{Si}$: Si, 5.7 and Br, 32.4%). The alcohol insoluble fraction was dried at 50°C under reduced pressure to yield 7g. of a substance melting at 228°C . (Found: Si, 8.3 and Br 16.0, Calc. for $\text{C}_{60}\text{H}_{46}\text{Br}_2\text{Si}_3$: Si, 8.3 and Br 15.8%). The infrared spectra of these substances are almost identical.

B. Reactions of Diphenyldichlorosilane and Lithium Biphenyl Compounds:

a. Synthesis of 4,4'-Bis[p-bromo-p'-biphenyl(diphenyl)silyl] biphenyl (II):

The reaction of 46.8g (0.15 mole) of 4,4'-dibromobiphenyl with 8.3g. (0.13 mole) of n-butyllithium followed by the dropwise addition to the mixture of 25.1g. (0.1 mole) of diphenyldichlorosilane gave II, a light-brown, ether insoluble solid substance, (Found: Si, 5.6 and Br, 16.3; Calc. for $\text{C}_{60}\text{H}_{44}\text{Br}_2\text{Si}_2$: Si, 5.7 and Br, 16.3%).

b. Synthesis of Linear Silbiphenylene Polymer and p-Bromo-p'-biphenyl-p-butyl-p'-biphenyldiphenylsilane (III):

A solution comprised of 25.0g (0.08 mole) of recrystallized (from toluene) 4,4'-dibromobiphenyl in 350 ml. of sodium-dried and redistilled benzene was added dropwise during about 3 hrs. to 11.3g (0.176 mole) of n-butyllithium dissolved in hexane (1 molar solution) at 58°C under a nitrogen atmosphere. A 10 ml. aliquot sample of the reaction product was added to a mixture of dry-ice and ether to give only the dicarboxylic acid derivative of biphenyl. Then, 32.0g. (0.126 mole) of diphenyldichlorosilane was added dropwise during 1 hr. to the reaction mixture at 58°C . After remaining overnight at room temperature, Color Test 116 was negative. About 65% of the product obtained from the reaction of 60g. (0.19 mole) of 4,4'-dibromobiphenyl and 12.3g. (0.19 mole) of n-butyllithium at 82°C was then added dropwise during 1 hr. to the initial reaction mixture. The final mixture was heated at 82°C for 3 hrs., allowed to stand at room temperature for about 72 hrs., hydrolyzed with 5% H_2SO_4 , and separated with ether to give 70g. of crude material. The crude product was washed with distilled H_2O , dried at 110°C , and extracted with boiling ether to yield 28.6g. of a very light-yellow, hard, ether insoluble resinous fraction containing 7.0 and 8.6% of silicon and bromine, respectively. The polymeric substance has a probable molecular configuration of $\text{p-BrC}_6\text{H}_4\text{C}_6\text{H}_4\text{-(C}_6\text{H}_5)_2\text{SiC}_6\text{H}_4\text{-Br-p}$, where n is about 4.5. The addition of petroleum ether to the ethyl ether soluble fraction precipitated about 85% of the crude material. The petroleum ether insoluble product was recrystallized from ethyl ether to give 12g. of III, a very-light yellow, hard solid substance.

c. Synthesis of Cyclic Silbiphenylene Polymer:

A mixture consisting of 46.8g. (0.15 mole) of 4,4'-dibromobiphenyl was treated under a nitrogen atmosphere for 16 hrs. at 75°C. At this time, Color Test I was positive. Then, 68.3g. (0.27 mole) of diphenyldichlorosilane was added to the mixture during 0.5 hr. and the ingredients were refluxed for 0.5 hr. after which time Color Test I was found to be negative. Lithium chloride was separated by filtering the mixture and the solvents were distilled off to give a crude bluish-black viscous liquid. The crude product was treated with petroleum ether to give 8.1g. of a greyish-white insoluble solid containing 8.2% of silicon. The petroleum ether soluble fraction contained 37.9g. (0.15 mole) of unreacted diphenyldichlorosilane and an oily product which was comprised mainly of a mixture of diphenylpolysiloxane and some n-butyl bromide.

C. Curing Studies:

Preselcted quantities of the curing agents were mixed with 0.50g. of polymer. The mixture was placed in a brass-ring mold, approximately 0.5 inch inside diameter and 0.25 inch high, and heated in a hydraulic press for 0.67-6.0 hrs. at 120-205°C. under a pressure about 4000 psi.

Since the resins under study are completely soluble in benzene, the degree of crosslinking was considered to be reflected by changes of solubility in this solvent. After the curing process, the treated specimens were extracted at reflux temperature with benzene and the amount of insoluble material was calculated by difference.

D. Thermogravimetric Analysis Measurements (TGA):

Approximately 0.2g. samples, accurately weighed to 0.1 mg. were placed in a Kanthal wire-wound furnace similar to that described in the literature¹⁷. The temperature of the furnace was reproducibly elevated at the desired rate by a motor-driven variable transformer. The residual weight and the temperature of the samples were recorded continuously during the entire heating period on an Ainsworth, two-pen, Type BYR-AU-A, semi-micro recording balance. Temperature measurements were made with a Pt/Pt-10% Rh thermocouple.

E. Infrared Measurements:

Infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam spectrophotometer. In general, the samples were observed over the 2.5-15 μ range in wazars on rock-salt prisms or in KBr pellets.

TABLE 1
EFFECTS OF CURING AGENTS
on
LINEAR SILBIPHENYLENE POLYMER *

<u>Curing Agent</u>	<u>Concentration (P.H.R.) **</u>	<u>Temperature (°C)</u>	<u>Time (Hr.)</u>	<u>Degree of Crosslinking (% Benzene Insol.)</u>
FeCl ₃	3.0	120	0.67	9.5
Benzoyl Peroxide	2.0	140	0.67	9.4
Benzoyl Peroxide/PbO	2.0/1.0	140	0.67	3.5
Benzoyl Peroxide/Cobalt Naphthenate	3.0/3.0	140	6.0	4.0
Benzoyl Peroxide/Cobalt Naphthenate	3.0/10.0	140	6.0	3.7
Benzoyl Peroxide/Cobalt Naphthenate	2.0/1.0	140	0.67	27.2
Benzoyl Peroxide/Cobalt Naphthenate	2.0/3.0	160	0.67	22.4
Benzoyl Peroxide/Cobalt Naphthenate	2.0/3.0	205	1.0	6.5

* All specimens were treated at a platen pressure of about 4000 psi.

** P.H.R. refers to parts per 100 parts of resin.

TABLE 2

EFFECTS OF CURING AGENTS
on
PERPHENYLATED SILOXANE POLYMER *

<u>Curing Agent</u>	<u>Concentration (P.H.R.) **</u>	<u>Temperature (°C)</u>	<u>Time (Hr.)</u>	<u>Degree of Crosslinking (% Benzene Insol.)</u>
Benzoyl Peroxide	2.0	140	0.67	1.9
Benzoyl Peroxide/Cobalt Naphthenate	2.0/1.0	140	0.67	5.0
Benzoyl Peroxide/Cobalt Naphthenate	2.0/3.0	205	0.67	4.4
Benzoyl Peroxide/PbO	2.0/1.0	140	0.67	3.7
Al ₂ O ₃	4.0	205	0.67	0.5
TiO ₂	2.0	140	6.0	7.8
TiO ₂	2.0	205	1.0	4.0
TiO ₂	4.0	205	0.67	7.8
FeCl ₃	2.0	205	0.67	18.7
FeCl ₃	2.0	205	1.0	6.9
FeCl ₃	2.0	140	6.0	44.6
FeCl ₃	10.0	140	6.0	60.8

* All specimens were treated at a platen pressure of 4000 psi.

** P.H.R. refers to parts per 100 parts of resin.

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